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THERMAL DECOMPOSITION OF DIMETHOXYMETHANE ELECTROLYTE SOLUTION.(U)

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THERMAL DECOMPOSITION OF DIMETHOXYMETHANE  
ELECTROLYTE SOLUTION

by

J. S. Foos and V. Meltz

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in the

Journal of the Electrochemical Society

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Abstract (continued)

NMR spectroscopy. A chain reaction mechanism is proposed for the decomposition which postulates oxygen-stabilized carbocation intermediates. Because the reaction may be impurity initiated and is quenched by Li metal, the importance of purification and storage of electrolyte with Li, is emphasized.

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THERMAL DECOMPOSITION OF DIMETHOXYMETHANE  
ELECTROLYTE SOLUTION

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INTRODUCTION

Ethereal solutions of  $\text{LiAsF}_6$  have shown promise for use as electrolytes in lithium batteries. Solution of  $\text{LiAsF}_6$  in 2-methyltetrahydrofuran (2Me-THF) and in ether blends with diethylether (DEE) have demonstrated the ability to cycle lithium in high efficiency in  $\text{Li/TiS}_2$  laboratory cells (1,2).

The ability of 2Me-THF electrolyte to cycle Li well is reflected in the superior thermal stability toward Li in storage tests at  $70^\circ\text{C}$  (3). Tetrahydrofuran (THF) electrolyte, which reacts with Li on storage, appears to react with Li in  $\text{Li/TiS}_2$  cells when it is used as a component of a blend with a less reactive ether (4). Although the reactivity observed in the above tests has been attributed to reaction with Li, many ether electrolytes also react at elevated temperatures ( $100^\circ\text{C}$ ) in the absence of Li (5). The reaction observed in  $\text{LiAsF}_6$  solutions is a dark brown coloration frequently accompanied by a white precipitate. In the case of DEE/ $\text{LiAsF}_6$  electrolytes, ethylene is formed (along with  $\text{H}_2$  in the presence of Li) (2). The reaction products were identified as containing As, implicating the  $\text{AsF}_6^-$  as a reactive species. The Li ion was implicated as a necessary catalytic species (4). In some cases, Li metal was found to suppress decomposition (5).

During the investigation of various ethers for use as electrolytic solvents in lithium batteries, dimethoxymethane (DMM) was chosen for testing (6). Storage tests at 70°C were conducted with solutions of LiAsF<sub>6</sub> in DMM in the presence and absence of Li. The visual results with this ether are similar to those previously reported for other ethers.

However, dramatic differences were observed for ether reactivity which are detected only through analysis of the reaction products. The simple structure of DMM and its decomposition products allow the use of NMR spectroscopy in determining the stoichiometry of its decomposition reaction. A mechanism for the decomposition is proposed based on the identity of the reaction products and the ratio in which they are produced.

#### EXPERIMENTAL

##### General

All purification procedures subsequent to distillation and storage test preparations were conducted at ambient temperature under Ar atmosphere in a Vacuum-Atmospheres Corp. dry box equipped with a Model He-493 Dri-Train.

##### Materials

The DMM (Aldrich) was dried with MgSO<sub>4</sub>, followed by molecular sieves. The solvent was then distilled from Na benzophenone ketyl. The lithium hexafluoroarsenate (LiAsF<sub>6</sub>) (U.S. Steel Agri-Chemicals, electrochemical grade) was used as-received. Lithium foil (15 mil) was obtained from Foote Mineral Company sealed under Ar.

Activated neutral alumina (Woelm 200 neutral, activity grade Super 1) was used as-received and exposed only to the dry box atmosphere. Approximately 1 g desiccant per 5 ml solvent was used in a given purification procedure.

The electrolytes for storage tests were prepared using  $\text{LiAsF}_6$  with cooling using Cu shot previously cooled in dry ice. The solvents, if treated with alumina, were passed through a column of activated alumina and the first 10% discarded.

#### Storage Tests

Generally, the stability tests were conducted by storing a sample of electrolyte (3-10 ml) at  $70^\circ\text{C}$  in the absence or presence of Li ( $1-2 \text{ cm}^2$ ). The sample was contained in screw-cap test tubes with Teflon-lined screw caps. The threads of the test tube were wrapped with Teflon tape.

The DMM electrolyte storage test which was analyzed by NMR spectroscopy was conducted in a 5 mm (0.8 mm wall) NMR tubes. The sample was placed in the tube in the dry box and then attached a vacuum line. The sample was outgassed in three freeze-thaw cycles and then the tube sealed under vacuum while the sample was frozen in liquid nitrogen ( $\text{LN}_2$ ).

#### Analyses

The test tube storage samples were analyzed by IR spectroscopy (Beckman Acculab 5) using a 10 cm gas cell (at  $\sim 20$  torr). The sample was first frozen ( $\text{LN}_2$ ) and then quickly fitted with an adapter which could be attached to a vacuum line. The sample was then allowed to warm and aliquots collected in the IR cell.

The proton NMR analyses were done using a JEOL FX-90Q spectrometer (Biomeasure Inc., Hopkinton, MA). The sample in a 5 mm NMR tube was supported in a 10 mm NMR tube using a Teflon spacer. This outer tube contained the deuteriochloroform for the deuterium lock and the tetramethylsilane (TMS) external standard. The chemical shifts are reported as ppm downfield from TMS. To determine the effect of the external TMS on chemical shift values, spectra of DMM solvent were run with internal and external TMS. The chemical shifts were  $\delta 3.26(6H)$  and  $\delta 4.47(2H)$  with internal TMS; and  $\delta 2.74(6H)$  and  $\delta 3.95(2H)$  with external TMS, giving a change of  $-0.52$  ppm with external TMS.

#### RESULTS

Stability tests were carried out with solutions of 1.5M  $LiAsF_6$  in DMM at  $70^\circ C$  with and without Li metal. The samples containing Li showed relatively little reaction, with the best samples showing no reaction after 30 days. The most stable samples appeared to be those prepared from distilled solvent which was subsequently treated with alumina (DA).

In contrast, when samples were stored without Li, the (DA) samples turned dark in 5 to 7 days. Samples which had not been treated with alumina (D) remained colorless from 11 to 17 days. In either case it is clear that the DMM electrolyte solution is stabilized by Li.

#### IR Analysis

A sample of DMM electrolyte that had turned dark due to storage at  $70^\circ C$  was analyzed by IR spectroscopy. This analysis was done by slowly warming the cooled sample which was attached to a vacuum line. Aliquots of



the vapor which were collected in the vacuum line were then analyzed in an IR gas cell. Surprisingly the sample was found to contain little or no DMM. The IR spectra contained only absorptions which are attributed to methyl formate, dimethyl ether, and combination of the two. The methyl formate absorptions were identical to those obtained from an authentic sample (Eastman). The dimethyl ether absorptions were identical to a published spectrum (7).

#### Proton NMR Analysis

In order to positively identify the products, to assess the stoichiometry of the reaction, and to search for minor products; the decomposition was repeated in an NMR tube. A sample of 1.5M LiAsF<sub>6</sub>/DMM was sealed in a 5 mm NMR tube which was stored at 70°C. At time intervals, the sample was removed and analyzed by proton NMR spectroscopy. The initial and final spectra are shown in Figure 1. At the top of Figure 1 is the spectrum of fresh DMM/LiAsF<sub>6</sub> electrolyte with peaks at  $\delta 4.19$  (s, 2H) and  $\delta 2.96$  (s, 6H). At the bottom is the spectrum showing a small amount of residual DMM along with methyl formate [ $\delta 7.59$  (d, J < 1 Hz, 1H) and  $\delta 3.25$  (m, J < 1 Hz, 3H)] and dimethyl ether [ $\delta 2.81$  (s, 6H)].

The chemical shifts for DMM methyl formate, and dimethyl ether observed above are listed in Table 1. This table also shows that when authentic methyl formate is added to DMM electrolyte solution, the chemical shift values of the methyl formate are near those attributed to the methyl formate in the storage test. It can be noted that as the amount of DMM in the sample decreases, the chemical shifts decrease in value. At the end of

the experiment, methyl formate and dimethyl ether were present in a 1:2 ratio as determined from integration of the NMR absorptions. The experiment is summarized in Table 2.

This experiment establishes that the decomposition gives almost exclusively 1 mole of methyl formate and 2 moles of dimethyl ether. The balanced equation for this reaction is shown in Equation 1.

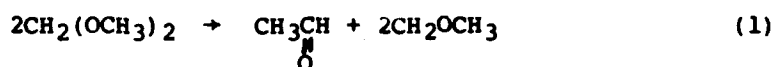


Table 2 shows that the brown color may be associated with the beginning of the decomposition of DMM. In contrast, a sample of LiAsF<sub>6</sub>/2Me THF electrolyte solution which had turned brown as a result of storage at 70°C, showed no trace of 2Me-THF decomposition when analyzed by proton NMR spectroscopy.

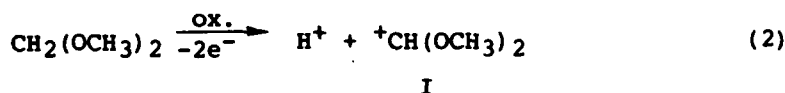
#### DISCUSSION

The dark coloration is typically observed when LiAsF<sub>6</sub>-ether solutions are stored at elevated temperatures. This coloration is not observed in storage tests with LiClO<sub>4</sub> (5) implying that the color is associated with the salt not the ether. Additionally, it has been observed that the time of onset of color depends on the purification technique used in preparing solvent, e.g., DMM/LiAsF<sub>6</sub> (DA) reacts more rapidly than DMM/LiAsF<sub>6</sub> (D). These observations imply that the color is a result of decomposition of AsF<sub>6</sub><sup>-</sup> and that this decomposition is affected by impurities remaining after solvent purification or due to solvent decomposition. The decomposition products of AsF<sub>6</sub><sup>-</sup> would be expected to be acidic and/or strongly oxidizing.

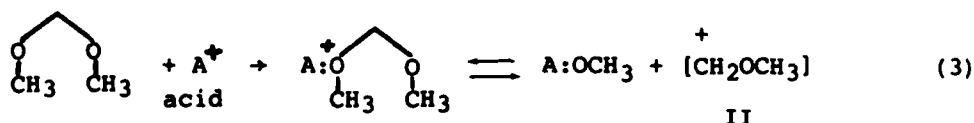
The polymerization of dioxolane is rapid in the presence of  $\text{LiAsF}_6$ , due to the influence of the  $\text{AsF}_6^-$  anion (9). This polymerization presumably operates in a cationic mechanism.

The above considerations imply that a cationic mechanism might be used to explain the decomposition of DMM to methyl formate and dimethyl ether. The observation that the presence of Li metal retards the decomposition reaction is consistent with this hypothesis.

Treatment of DMM with an oxidizing agent would be expected to give an oxygen stabilized cation, especially in the absence of strong nucleophile (10). It is important to note that the prominent nucleophiles in the DMM- $\text{LiAsF}_6$  solution are the  $\text{AsF}_6^-$  anion, which would be poorly nucleophilic (the anion of a strong acid), and the ether itself. The expected cation, I, would be stabilized by presence of two oxygen atoms, Equation 2.

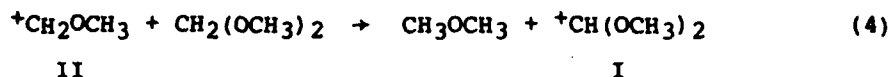


Alternately, the cation I could also be formed from acidic impurities. The instability of acetals like DMM is well known in acidic aqueous solution. In the absence of  $\text{H}_2\text{O}$ , an additional molecule of solvent might be expected to react with an acid-base (ether) complex, Equation 3, to give the dimethyl ether cation (II).

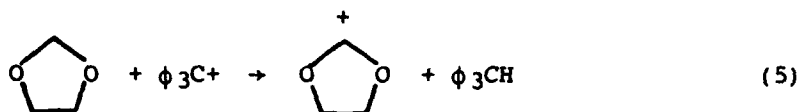


This cation would undoubtedly exist in solution in the form of an oxonium ion formed with a molecule of solvent (11). However, it also might react

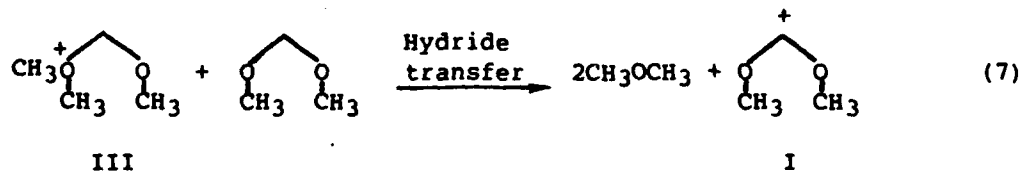
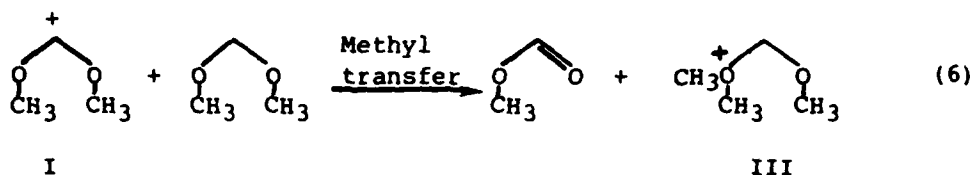
with DMM via hydride transfer to give the same stabilized intermediate, I, described above, see Equation 4:



A similar reaction was used to form the 1,3-dioxolan-2-ylum ion (II), (Equation 5):

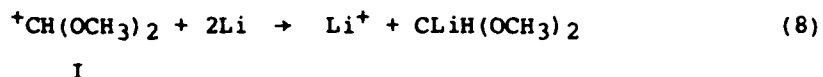


The cation I, although relatively stable, may decompose by methyl transfer to a solvent molecule, forming an oxonium ion (III). This oxonium ion could in turn decompose (with a hydride transfer), regenerating the cation I. These reactions are shown in Equations 6 and 7 and constitute the propagation steps of a chain reaction.



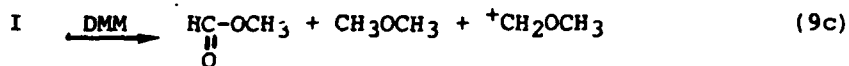
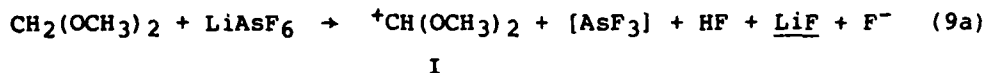
The reactions described in Equations 2-4 are the initiation step.

This mechanism explains the products and stoichiometry observed. It also explains the reaction retarding effect of Li metal. It would be expected that cation intermediates would be rapidly reduced on Li to anions which might be insoluble but which would at least disrupt the propagation of the chain reaction, Equation 8:



Nucleophilic impurities such as  $\text{H}_2\text{O}$  would be expected to react rapidly with cations to disrupt the chain. Such reactions would be chain terminating steps.

An alternate mechanism for the reaction which might be proposed is the direct oxidation of DMM by  $\text{AsF}_6^-$  (or  $\text{AsF}_6^-$  decomposition product). It has been suggested that in the case of several ethers (not DMM) that the reactive agent may be  $\text{AsF}_5$  produced from the thermal decomposition of  $\text{LiAsF}_6$  (4,5). This corresponds to an initiation step of the chain mechanism. This reaction may become the principal route of decomposition if suitably catalyzed or in the presence of an ether less amenable than DMM to a chain reaction. This reaction sequence is shown in Equations 9a-c.



In our view, this mechanism fails to explain the observed DMM decomposition for several reasons. Thus, although a small amount of white precipitate is

observed, it is too little to be the LiF produced according to Equation 9a if that were the major reaction. Actually, the amount of LiAsF<sub>6</sub> in 1.5M LiAsF<sub>6</sub>/DMM is insufficient to oxidize the DMM present by this reaction. The IR spectrum of the residual salt left after the decomposition of DMM in a storage test showed a strong peak remaining at 700 cm<sup>-1</sup>, which corresponds to the AsF<sub>6</sub><sup>-</sup> absorption. Significant oxidation by LiAsF<sub>6</sub> would not be expected in view of its apparent good thermal and solution stability (12).

In addition, no appreciable absorption was observed in the proton NMR spectra which could be attributed to the organofluorine compound in Equation 9b. We note too that the reaction in Equation 9c, an initiation step in the proposed chain, does not have the right stoichiometry to give the observed products.

A free-radical mechanism might be proposed as an alternative to the cation mechanism suggested above. However, we do not believe that this is credible. Cation intermediates of the type proposed are known to be stable species whereas similar free-radical species would be much less stable. Also, they would show coupling products.

#### CONCLUSIONS

It is observed that DMM electrolyte decomposes thermally to give dimethyl ether and methyl formate. Since methyl formate is unstable towards Li (13) it would be expected that this reaction would seriously degrade the performance of DMM/LiAsF<sub>6</sub> electrolyte in a Li cell. This decomposition reaction may occur during electrolyte preparation or during storage prior to filling the cell.

In the cell, in the presence of the Li negative, the decomposition could be minimized. However, in the bulk solution, away from the surface of the Li, some decomposition may be initiated by acidic, or oxidizing, impurities introduced during the construction of the cell. If a reaction in the cell, such as  $\text{AsF}_6^-$  decomposition, produces an acid or oxidizing agent, the effects of that reaction will be magnified by the DMM decomposition chain reaction.

More generally, this reaction is an illustration of a type of reaction that can occur only in certain specialized conditions. This condition includes the presence of a non-reactive, non-nucleophilic anion, i.e.,  $\text{AsF}_6^-$ , which may stabilize the carbocation intermediates. Required as well is the absence of a reactive nucleophile other than the solvent itself. These conditions are seldom achieved in synthetic organic chemistry but are typical in Li battery electrolytes.

# REFERENCES

1. G. L. Holleck, K. M. Abraham and S. B. Brummer in Proceedings of the Symposia on Power Sources for Biomedical Implantable Applications and Ambient Temperature Lithium Batteries, B. B. Owens and N. Margalit, eds., Vol. 80-4, The Electrochemical Society, Pennington, NJ, 384 (1980).
2. K. M. Abraham, J. L. Goldman and D. L. Natwig, J. Electrochem. Soc., submitted.
3. J. L. Goldman, R. M. Mank, J. H. Young and V. R. Koch, J. Electrochem. Soc., 127, 1461 (1980).
4. K. M. Abraham and J. L. Goldman, Prepared for publication in the Journal of Power Sources.
5. V. R. Koch, J. L. Goldman, J. T. Y. Maurand, and M. Mulvaney, Proceedings of the Symposium on Lithium Batteries, H. V. Venkatesetty, ed., Vol. 81-4, The Electrochemical Society, Pennington, NJ.
6. J. S. Foos, K. M. Abraham, J. McVeigh, J. L. Goldman, and V. Meltz, submitted for presentation at the Fall Meeting of the Electrochemical Society, Detroit, MI, October (1982).
7. Raman/IR Atlas of Organic Compounds, Ed. by B. Schroder and W. Meier, Verlag Chemie, Weinheim, West Germany (1977).
8. The Aldrich Library of NMR Spectra, Aldrich Chemical Co. (1974).
9. P. G. Glugla in Proceedings of the Symposia on Power Sources for Biomedical Implantable Applications and Ambient Temperature Lithium Batteries, B. B. Owens and N. Margalit, eds., Vol. 8-4, The Electrochemical Society, Pennington, NJ, 407 (1980).
10. V. D. Parker in Organic Electrochemistry, ed. by M. M. Baizer, Dekker, New York (1973) pp. 544-5.
11. P. Kubisa and S. Penczek, Makromol. Chem., 144, 169 (1971).
12. R. C. Cannon, C. C. Stone, and R. A. Wiesboeck, in Proceedings of the Symposia on Power Sources for Biomedical Implantable Applications and Ambient Temperature Lithium Batteries, B. B. Owens and N. Margalit, eds., Vol. 80-4, The Electrochemical Society, Pennington, NJ, p. 321 (1980).
13. R. D. Rauh and S. B. Brummer, Electrochimica Acta, 22, 85 (1977).



TABLE 1

OBSERVED CHEMICAL SHIFTS (ppm,  $\delta$ ) FOR DMM, METHYL FORMATE, AND DIMETHYL ETHER (vs. EXTERNAL TMS) IN 1.5M LiAsF<sub>6</sub>/DMM STORAGE TEST, REFERENCE SAMPLE, AND DMM SOLVENT ONLY.

|                | 1.5M LiAsF <sub>6</sub> /DMM Storage Sample (70°C) |                        |                        | Reference Sample  |                        |
|----------------|--|------------------------|------------------------|---|------------------------|
|                | Initial  | 35% Decomposed         | 90% Decomposed         | Methyl Formate<br>Added to 1.5M LiAsF <sub>6</sub> /DMM | DMM<br>Solvent Only*   |
| DMM            | 2.96 (6H)<br>4.19 (2H)                             | 2.92 (6H)<br>4.14 (2H) | 2.81 (6H)<br>4.02 (2H) | 2.94 (6H)<br>4.16 (2H)                                  | 2.74 (6H)<br>3.95 (2H) |
| Methyl Formate | -<br>-   | 3.39 (3H)<br>7.70 (1H) | 3.25 (3H)<br>7.59 (1H) | 3.41 (3H)<br>7.75 (1H)                                  | -<br>-                 |
| Dimethyl Ether | -  | 2.94 (6H)              | 2.81 (6H)              | -   | -                      |

\*The chemical shift difference between these values and literature values (3.40 and 4.58, Ref. 8) is primarily the result of -0.52 ppm change due to the placement of TMS external to the sample (see Experimental).

TABLE 2

VISUAL AND PROTON NMR SPECTROSCOPIC ANALYSIS OF  $\text{LiAsF}_6/\text{DMM}$  STORED AT  $70^\circ\text{C}$ .

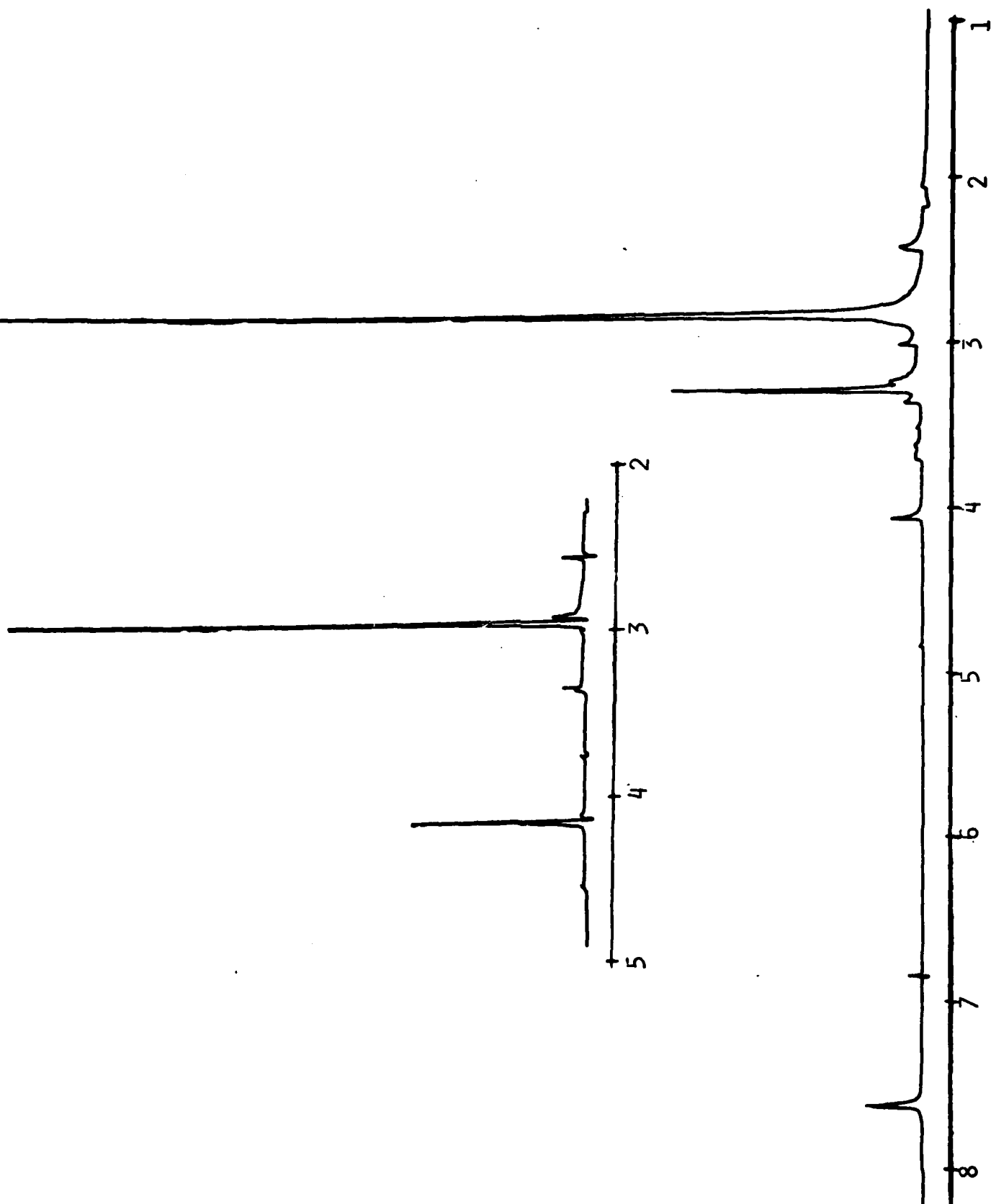
| <u>Time (days)</u> | <u>Color</u>           | <u>Percent Decomposition*</u> |
|--------------------|------------------------|-------------------------------|
| 0                  | Clear-colorless        | 0                             |
| 5                  | Clear-colorless        | 0                             |
| 9                  | Dark brown             | ~35                           |
| 16                 | Dark brown (white ppt) | ~90                           |

\*Based on ratio of DMM to methyl formate.

FIGURE CAPTION

Fig. 1. Proton NMR spectra. Top: Freshly prepared DMM/LiAsF<sub>6</sub>.  
Bottom: DMM/LiAsF<sub>6</sub> after 16 days at 70°C.

FIG. 1



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